

УДК 537.312

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INFLUENCE OF FRACTIONAL STRUCTURE OF THE GRANULATED NANOFIBROUS CARBON FILLER ON ELECTROPHYSICAL PROPERTIES OF EPOXY COMPOSITES

The effect of fractional structure of the granulated nanofiber carbon filler on the electrical properties of epoxy resin composites has been investigated in this article. The conductivity and permittivity of composite materials has been measured in the frequency range of 100 Hz – 1 MHz. It was shown that the grain-size distribution of the applied filler effects the electrical properties of epoxy resin / carbon nanofiber composites.

Introduction. Carbon nanomaterials are of the great interest for many researchers all over the world. In the number of references in the scientific literature the leading place is occupied by the carbon nanotubes (CNTS) and carbon nanofibers (CNF). Due to the wide range of interesting properties such as high strength, high electrical and thermal conductivity, these types of carbon nanomaterials have prospects of application in many fields, in particular as catalysts and carriers of catalysts [1, 2], fillers for polymer composites [3–4] electrochemical sensors [5], electrode materials for supercode-Satoru [6–7] and others. In the recent years, the increasing attention is paid to the study of the properties of composite materials on the basis of CNF, the perspectives of their application are associated with cheapness and ease of access, which is important in the case of creation of the industrial production of these materials.

Among the wide range of scientific problems of creating polymer composites based on CNF the important issue is to develop a method of producing epoxy composites with improved properties. In particular, the method of producing the composite affects the dispersion of the filler and its distribution in the polymer matrix [8]. In the work [9] the effect of various methods of obtaining epoxy composites (mechanical stirring, ultrasonic dispersion in a solvent and epoxy resin) on their electrophysical properties was investigated.

In the work [10] it was found that the dispersion of the filler has a significant impact on the electrophysical properties of the composites. Similar effects have been published by Cardoso and his colleagues in the work [11].

In the work [12], the authors used two methods of obtaining composites using ultrasonic dispersion UNV in the system solvent – epoxy resin. It was found that the method of introduction of the epoxy resin at receiving the composite significant-

ly affects the stealth properties of composites in the field of 8–20 GHz.

In the work [13] the authors use electric fields to produce composites of epoxy resin CNF with anisotropic properties. The formation of the conductive network of the filler in the direction of application of electric field allows to control the electrical conductivity of the composites successfully.

Unlike most of the works where powdered nanofibers filters were used, in this work as a filler is used granulated nanofibrous carbon filler.

In this paper the influence of the fractional composition of granulated nanofibrous carbon filler on the electrophysical properties of epoxy composites was found.

The experimental technique. Nanofibrous granular material NWU-1 (Fig. 1) used in this work was obtained by catalytic decomposition of methane in PI-pilot reactor with vibramicina layer [14].



Fig. 1. The appearance of the granules NWU-1

Micropictures, which were obtained using transmission electron microscopy, is shown in Fig. 2.

For sample preparation of composite materials was used epoxy resin (ES) of the brand DER 331 (DOW Chemicals Co.) and curing the polyethyle-

nepolyamine (Pepa) (CJSC "Uralkhimplast"). The resin and hardener were mixed in a mass ratio of 6 : 1. A sample NWU-1 was divided into fractions using a set of laboratory sieves. A given fraction of NWU-1 was mixed with ES.

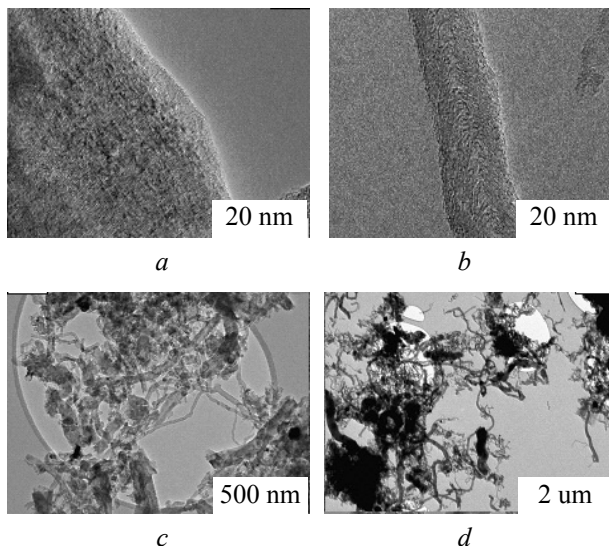


Fig. 2. Images of the sample of granular nanofibrous carbon material with different magnification (a–d)

The composites samples have been obtained with concentration of NWU-1 (p) 10 wt %. Separate fractions of NWU-1, as well as their mixtures, were used as filler. For detailed consideration the following samples of composites with different fractional composition of the filler (Table).

Fractional composition of the sample of filler NWU-1 and its concentration in the composite

Sample number	Particles size used in fraction nwu-1, mkm	Concentration of nwu-1 in the composite, wt %
1	63–80	10
2	315–500	10
3	100–315	6.67
	315–500	3.33
4	80–100	3.33
	100–315	6.67
5	80–100	10
6	<100	10

Frequency dependence of electrical conductivity, dielectric permittivity and tangent of dielectric loss of the composites were determined on the analyzer dielectric properties and impedance Novo-control Beta K at room temperature in the frequency range 0.09 Hz – 1 MHz.

Samples of composite materials had a cylindrical shape. The height and diameter of the samples was 3–5 and 31.4 mm, respectively.

The specific volume electrical conductivity was determined by formula (1):

$$\sigma = \frac{h \cdot G}{S}, \quad (1)$$

where σ – the conductivity, Cm/m; G – the sample conductivity, Cm; S – sample area (m²); h – is the sample thickness, m.

The dielectric constant was determined by using the expression (2):

$$\varepsilon = \frac{C \cdot h}{\varepsilon_0 \cdot S}, \quad (2)$$

where ε – the dielectric constant of the sample; ε_0 – the permittivity of vacuum, $\varepsilon_0 = 8.85 \cdot 10^{-12}$ f/m; C – the capacitance of the sample F.

Main part. Because the original sample NWU-1 is a granular material with a particle size in the range of 0.05 to 8 mm, the particle size of this filler can greatly influence the conductivity and permittivity of composites.

The conductivity of the composites ES/CNF-1 with a filler different fractional composition with the content of 10 wt % ranged 10–5–10–9 Cm/m. The filler in this case is a mixture of larger particles 315–500 mkm with a grain size 100–315 mkm in the proportion of 1 : 2. As the conductivity of the samples No 2 is the worst among all the studied compositions, the introduction of the particles with smaller fractions 100–315 mkm into the filler increases the conductivity by reducing the effective

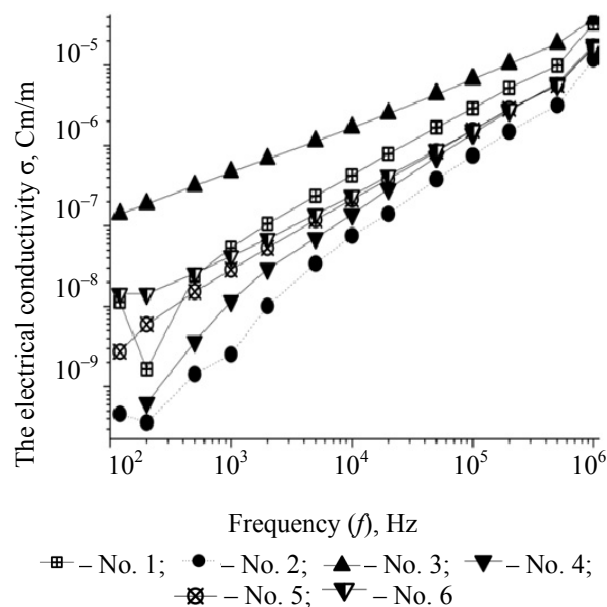


Fig. 3. The influence of the fractional composition of NWU-1 on the electrical conductivity of the composite ES / NWU-1

When considering samples that were obtained without the using of mixtures of fractions it is seen that the sample with particles of NWU-1 size

63–80 mkm possessed the best electrophysical properties. To improve the conductivity of the composites a mixture of coating 80–100 and 100–315 mkm, and 100–315 and 315–500 mkm were used as a filler. The composite with addition of a mixture of fractions 100–315 mkm and 315–500 mkm (sample No 3) possessed the highest conductivity.

Figure 4 presents the dependence of the dielectric permittivity of the composites from the fractional composition of the filler. The dielectric constant (ϵ) of the composite with the fraction 315–500 mkm NWU-1 (sample No. 2) practically doesn't depend on frequency, that indicates a weak contribution of interfacial polarization due to the formation of low surface interface between matrix and filler. A similar behavior of $\epsilon(f)$ presents in all other samples with addition of fractions 80–100 mkm, <100 mkm and mixture fractions 80–100 and 100–315 mkm. Despite the weak dependence of the dielectric constant on frequency, sample No. 1 (contains particles 63–80 mkm) has a higher high-frequency dielectric constant $\epsilon_{\infty} = 15$. Sample No. 3 (filled with a mixture of fractions 100–315 and 315–500 mkm) despite the improved conductivity shows a small high frequency dielectric constant $\epsilon_{\infty} = 6$ at a concentration of 10 wt % and this value varies slightly with increasing frequency. For the latest composite it is characterised by the power dependence of $\epsilon(f)$ in the double logarithmic coordinates, indicating a greater contribution of interfacial effects in polarization processes. It may indicate that the filler in this case forms a large surface interface that contributes to the polarization at low frequencies, and this effect disappears with increasing frequency.

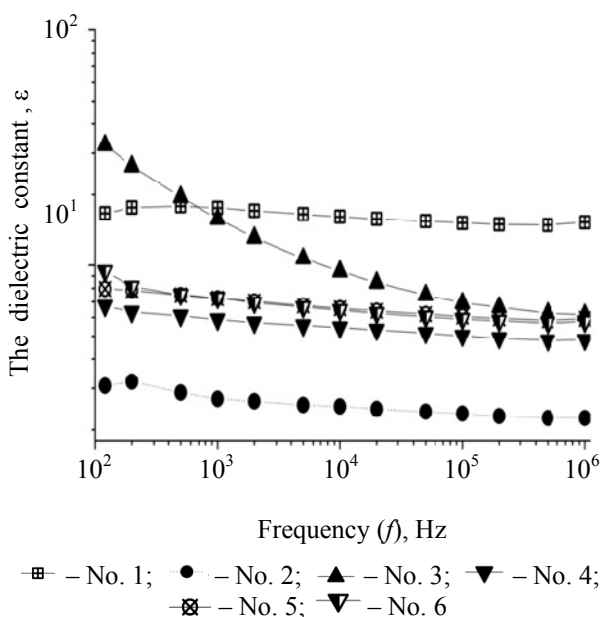


Fig. 4. The influence of the fractional composition of NWU-1 on the dielectric conductivity of the composite ES / NWU-1

In summary, we note that to increase the conductivity of epoxy composites, it is more efficient to use as a filler mixture of particles of NWU-1 size 100–315 mkm and 315–500 mkm with a higher proportion of fine fraction. To improve the high-frequency dielectric constant is preferable to use filler with a particle size 63–80 mkm. For comparison, the dielectric constant of the composite with the addition of particles less than 100 microns, with $p = 45\%$ (maximum concentration) is $\epsilon^{\infty} = 17$, which is not much higher than the permeability of the composite with the fraction 63–80 mkm ($\epsilon^{\infty} = 15$) at $p = 10\%$. Thus, selection of the optimal fractional composition of NWU-1 can provide a much higher dielectric constant of the composites with relatively low concentrations of the filler.

In conclusion it should be noted that the use of different fractions of granulated nanofibrous carbon filler to control the electro-physical properties of epoxy composites is quite effectively. Remember that to apply the material NWU-1 as a filler just the separation into fractions without the use of grinding filler must be used.

Conclusion. It was found that the use of a certain fractional composition of nanofibrous carbon filler is effective for improving the electrical properties against electromagnetic radiation. Use of a specific fractional composition enables to avoid costly manufacturing operations grinding.

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Received: 20.02 2014